# SYNTHESIS AND PROPERTIES OF A SYMMETRICAL MACROHETEROCYCLIC COMPOUND CONTAINING 1,3,4-THIADIAZOLE RESIDUES

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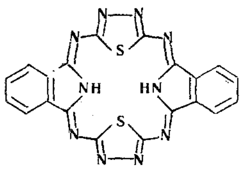
A new macroheterocyclic, symmetrical compound containing 1,3,4-thiadiazole residues was synthesized, and several of its physicochemical properties are given.

In [1] it was shown that symmetrical and unsymmetrical, macroheterocyclic compounds (macrocycles) can be obtained by replacement of one or two isoindole residues in phthalocyanin by residues of other cyclic compounds. The compounds of unsymmetrical structures have two absorption maxima, one in the near UV (340-350 nm) and one in the visible region of the spectrum (500-510 nm), and are purple.

The symmetrical compounds have one absorption maximum in the near UV region (340-360 nm) and are yellow. The higher color of the macrocycles, as compared with the color of phthalocyanin, is explained by the fact that their macrocycle, in contrast to the macrocycle of phthalocyanin, does not have a closed conjugation chain. The absence of the latter affects other properties of the macrocycles: they are more unstable than phthalocyanin, are readily hydrolyzed, and melt on heating. Their complexes with metals are also more unstable than metal–phthalocyanin complexes.

A red macroheterocyclic compound – 5,24:12,17-diaminodibenzo[c,m]-7,10:19,22-di(thiadiazolyl)-6,11,18,23-tetraazacycloekosine (I) – is obtained by the replacement in phthalocyanin of two isoindole residues by 1,3,4-thiadiazole residues.



As compared with the absorption maximum of phthalocyanin (703 nm), the absorption maximum in the spectrum of I (530 nm) is shifted to the short-wave region. This should apparently be explained by the fact that, in contrast to phthalocyanin, only two isoindole residues enter into the composition of I. It is well known that replacement of isoindole residues in phthalocyanin with pyrrole residues results in a shift in the absorption maximum to the short-wave region. Thus, for example, tribenzotetraazaporphine has an absorption maximum at 675 nm [2], while tetraazaporphine has an absorption maximum at 628 nm [3]. In addition, in contrast to the macrocycle of phthalocyanin, the alternation of carbon and nitrogen atoms is disrupted by the inclusion of sulfur atoms in the conjugation chain of the macrocycle of I. The inclusion of sulfur in the conjugation chain apparently affects the planar structure of the compound and its absorption spectrum. It is interesting to note that the replacement of the imino group in indigo, which is blue ($\lambda_{max}$ 591 nm), by sulfur atoms changes its color to red. Thioindigo has an absorption maximum at 540 nm.

The absorption maximum of I is considerably shifted to the long-wave region as compared with symmetrical macrocycles, where conjugation in the macrocycle is disrupted by benzene or pyridine residues. It is even somewhat farther in the long-wave region than in an unsymmetrical macrocycle (Fig. 1).

In contrast to other macrocycles, I dissolves in dilute alkali solutions. The solubility in alkali solutions is apparently associated with the presence of thiadiazole residues. The sulfur of the thiadiazole residues is converted to the tetravalent state by alkali with the addition of –OK groups, and one of the nitrogen atoms is converted to an imino group similar to the conversion of anthra[1,2-c][1,2,5]thiadiazole-6,11-

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dione [4]. The absorption spectrum of an alkaline solution of the macrocycle does not contain an absorption maximum in the visible region; this is associated with disruption of the conjugation chain of the macrocycle as a consequence of the formation of imino groups. The starting macrocycle is isolated by neutralization of the alkaline solution with acid. It was identified by spectroscopy in the UV, visible, and IR regions.

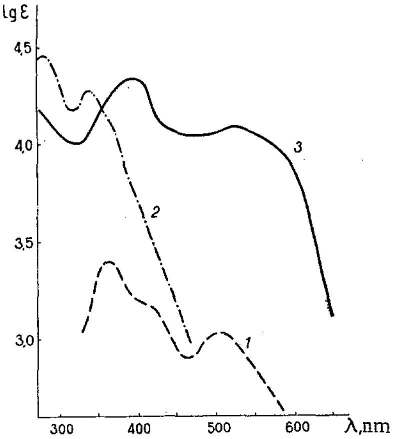
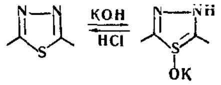


Fig. 1. Absorption spectra of macroheterocyclic compounds: 1) unsymmetrical macrocycle with one benzene residue; 2) symmetrical macrocycle with two benzene residues; 3) symmetrical macrocycle with two 1,3,4-thiadiazole residues.



## EXPERIMENTAL

Phthalonitrile [4.8 g (0.0375 mole)], 4.5 g (0.0387 mole) of 2,5-diamino-1,3,4-thiadiazole, and 55 ml of ethylene glycol were introduced into a flask equipped with a stirrer; and the mixture was heated at 120 deg for 20 h. The reaction mass was then cooled and diluted with 600 ml of water. The resulting dark-cherry precipitate was filtered, washed with water and alcohol, and dried to give 7.1 g (81%) of I, which was purified by extraction with methanol.

Compound I can also be obtained as follows. Sodium metal [0.04 g (0.00174 g-atom)] was dissolved in 20 ml of absolute butanol. 2,5-Diamino-1,3,4-thiadiazole [0.6 g (0.00517 mole)] and 0.62 g (0.00485 mole) of phthalonitrile were added to this solution; and the resulting mixture was held with vigorous stirring at 50 deg for 10 h, at 90 deg for 10 h, and, finally, refluxed for 20 h. The cooled reaction mass was filtered, and the crude product was washed with alcohol and water and dried to give 1.0 g (91%) of a dark-cherry product which did not melt up to 400 deg. Found %: C 52.4; H 2.2; N 30.5; S 13.6; mol. wt. 486 (ebullioscopy in dimethylformamide). $C_{20}H_{10}N_{10}S_2$. Calc. %: C 52.9; H 2.2; N 30.9; S 14.1; mol. wt. 454.4. The absorption maximum in dimethylformamide was 530 nm (log ε 4.08). The compound is very slightly soluble in alcohols and benzene and its homologs, partially soluble in dimethylformamide and pyridine, and soluble in concentrated mineral acids and dilute alkalis.

Hydrolysis of 0.6 g of the product in 25% hydrochloric acid at 90 deg for 4 h gave 0.41 g (93%) of phthalic acid with mp 190-191 deg. The filtrate was evaporated to dryness, the residue was dissolved in alcohol, and an alcohol solution of picric acid was added to give 1.4 g (94%) of the picrate of 2,5-diamino-1,3,4-thiadiazole with mp 260 deg.

## LITERATURE CITED

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